Metal-Organic Frameworks

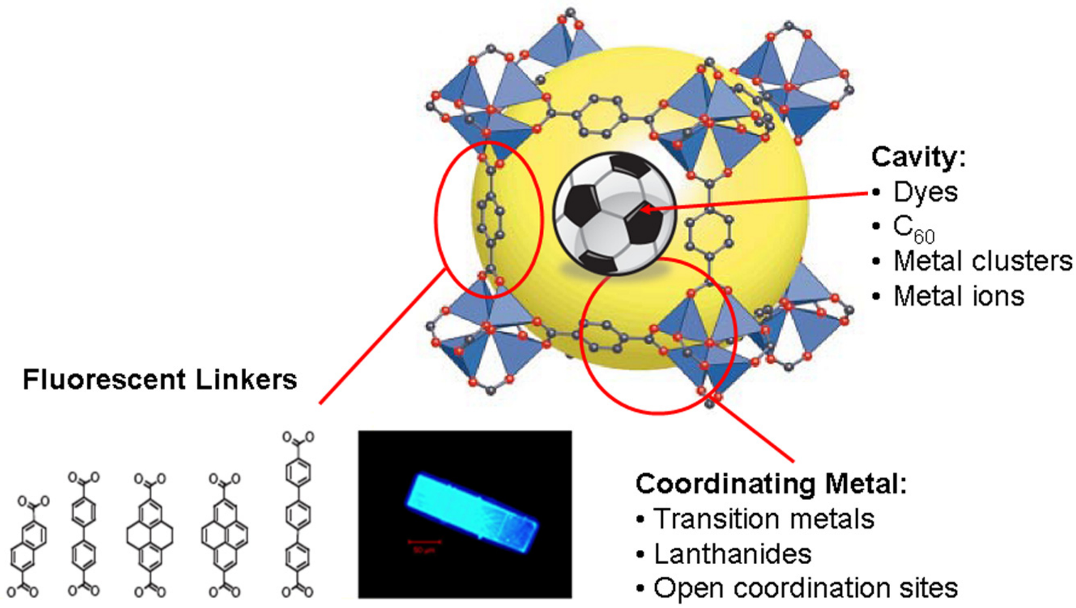

Figure 1: Potential sensing mechanisms in a typical MOF, illustrated using the classic MOF-5. This consists of Zn(II) ions (at the center of the blue tetrahedrons) linked by benzene dicarboxylate groups (black dots: carbon; red dots: oxygen). The yellow sphere represents the open space available for guest molecules.

Versatile nanoporous materials can be designed for diverse sensing applications

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The need for real-time, compact, and inexpensive sensors continues to grow in both complexity and urgency. Homeland security and defense applications such as portal monitoring, chemical weapon detection, radiation detection, and water quality monitoring have long been high priorities. Other newer applications include personal exposure monitors, sensors to provide advance warning of food spoilage, and breath analyzers that provide pre-symptomatic indication of infection. Development of these systems can be very demanding in several ways, requiring high levels of sensitivity and specificity in small, economical packages.

Novel nanoporous materials known as metal-organic frameworks (MOFs) are currently attracting considerable attention for a variety of sensing applications. They are ideal candidates because they have tailorable nanoporosity and ultrahigh surface areas. A typical MOF (Fig. 1) consists of metal cations such as Zn(II) linked by anionic organic groups such as carboxylates, yielding a rigid, open framework with cavities that can accommodate guest molecules. The metal ion framework can have open coordination sites to accommodate ligand binding. The organic linkers can consist of a variety of functional molecules, including fluorophores. The versatility of the combined framework and linkers allows these materials to function as sensors in a variety of ways, two of which are discussed below.

In the first example, a sensor is designed to take advantage of MOFs that can alter their unit cell dimensions by as much as 10% when guest molecules are adsorbed within the pores. Gas adsorption will

therefore cause distortions in a supported thin MOF film. This creates a novel transduction mechanism if, as depicted in Fig. 2, the substrate is a microcantilever that bends under interfacial stress. Thus the gas adsorption is detected via the stress-induced bending of the microcantilever that can be monitored by a very sensitive optical sensor or by a built-in piezoresistive stress sensor. Recently, this was demonstrated with a copper-containing MOF (Fig. 2). In its hydrated state, the MOF layer enables water vapor, methanol, and ethanol vapors to be detected to varying extents, with no response to N_2, O_2, or CO_2. In contrast, removing water bound to exchangeable sites on the MOF, as well as adsorbed within its pores, turns on sensitivity to CO_2. Thus MOFs can serve as effective recognition chemistries for a variety of gases and might be useful in a breath analysis or humidity sensing application.

In a second, very different, example, new MOFs containing the organic fluorophore stilbene dicarboxylate as a linker emit visible light on nanosecond timescales when irradiated with high-energy protons, alpha particles, and electrons (Figure 3). A completely new class of scintillation materials is created by this development, with the potential to rationally tailor properties for specific radiation detection applications. In general, the detection and identification of subatomic particles is an important scientific problem with implications for medical devices, radiography, biochemical analysis, particle physics, nuclear nonproliferation, and homeland security.

These two examples demonstrate that MOFs are indeed multifaceted. There are, however, many other MOFs that remain largely undeveloped as sensing materials. Research at Sandia therefore aims to realize this potential by both understanding the underlying mechanisms for sensing and by developing methods needed to integrate them with other materials and devices.

Figure 2: MOF-coated microcantilevers can be used to detect a variety of gases. In this case, the crystal lattice of the MOF CuBTC (copper ions linked by benzene tricarboxylate groups) expands or contracts when it adsorbs an analyte, creating measurable stress at the interface with a microcantilever.

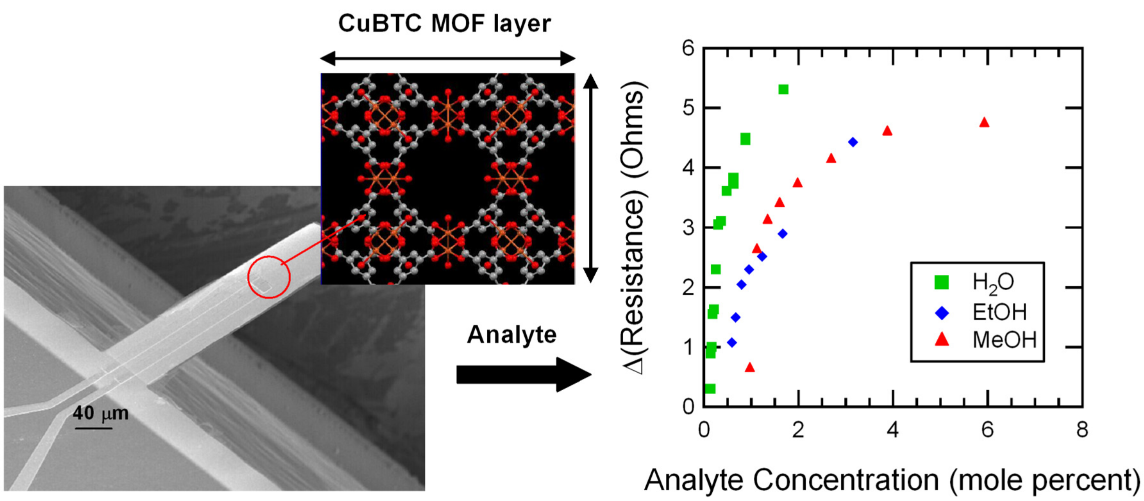
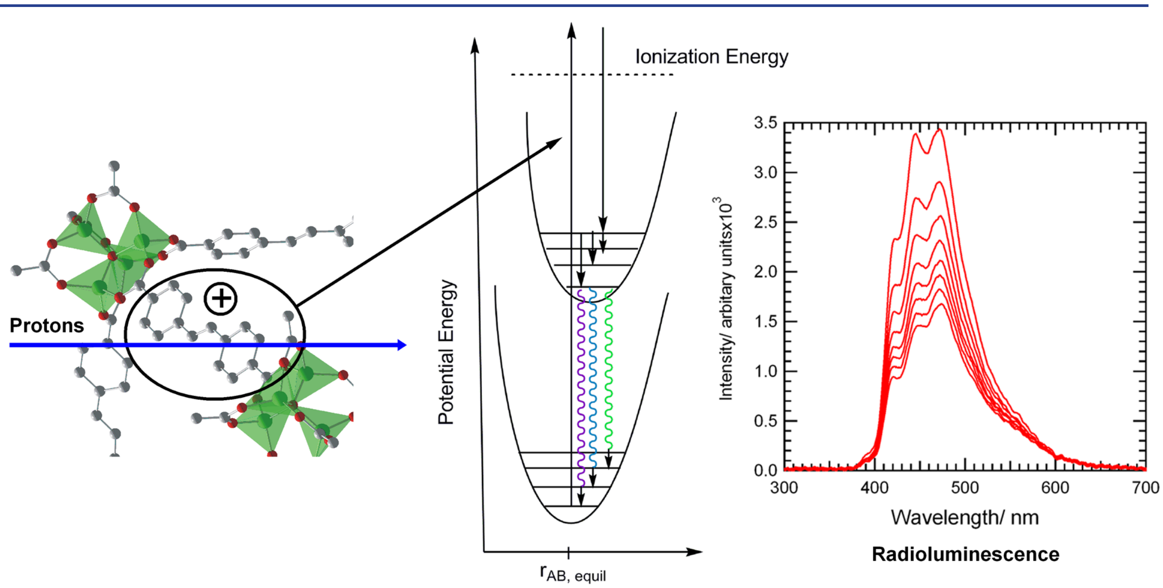


Figure 3: Schematic of scintillation induced by high-energy protons in a MOF.



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